

<p align="center">LLNL Environmental Restoration Division Standard Operating Procedure</p>	<p align="center">TITLE: Sampling for Volatile Organic Compounds</p>
<p>APPROVAL _____ Date _____</p> <p>Environmental Chemistry and Biology Group Leader</p>	<p align="center">PREPARERS: R. Goodrich, S. Gregory, G. Howard, and D. Rice</p> <p align="center">REVIEWERS: R. Brown*, T. Carlsen, E. Christofferson*, P. Daley, V. Dibley, J. Duarte, B. Failor*, J. Greci, B. Hoppes*, G. Howard, M. Ridley, and B. Ward*</p>
<p>APPROVAL _____ Date _____</p> <p>Division Leader</p> <p>CONCURRENCE _____ Date _____</p> <p>QA Implementation Coordinator</p>	<p align="center">PROCEDURE NUMBER: ERD SOP-2.6</p> <p align="center">REVISION: 2</p> <p align="center">EFFECTIVE DATE: December 1, 1995</p> <p align="center">Page 1 of 7</p>

*Operations and Regulatory Affairs Division

1.0 PURPOSE

To provide guidance on the collection of a ground water sample for trace volatile organic compounds (VOCs). The objective is to provide to the laboratory a sample representative of its original environment.

2.0 APPLICABILITY

This Standard Operating Procedure applies to the collection of ground water samples to be analyzed for VOCs. Due to the high volatility of such compounds as Trichloroethene, extra measures are implemented during sample collection and transport to maintain the sample in its pristine condition.

3.0 REFERENCES

- 3.1 Barcelona, M. J., J. A. Helfrich, and E. E. Garske (1985), "Sampling Tubing Effects on Groundwater Samples," *Analy. Chem.* **57**, pp. 460-463.

Procedure No. ERD SOP-2.6	Revision Number 2	Effective Date December 1, 1995	Page 2 of 7
------------------------------	----------------------	------------------------------------	-------------

- 3.2 Barcelona, M. J., J. A. Helfrich, E. E. Garske, and J. P. Gibb (1984), "A Laboratory Evaluation of Groundwater Sampling Mechanisms," *Groundwater Monitoring Review*, Spring, pp. 32-41.
- 3.3 Nielsen, D. M. and G. L. Yeates (1985), "A Comparison of Sampling Mechanisms Available for Small-Diameter Groundwater Monitoring Wells," *Groundwater Monitoring Review*, Spring, pp. 83-99.
- 3.4 U.S. EPA (1985), *Practical Guide for Groundwater Sampling*, Washington, D.C. (EPA/600/2-85/104).
- 3.5 U.S. EPA (1986), *RCRA Groundwater Monitoring Technical Enforcement Guidance Document*, Washington, D.C. (OSWER-9959.1).

4.0 DEFINITIONS

4.1 Volatile Organic Compounds (VOCs)

A group of organic compounds characterized by their tendency to evaporate easily at room temperature. Some familiar substances containing VOCs are solvents, gasoline, paint thinners, and nail polish remover.

5.0 RESPONSIBILITIES

5.1 Division Leader

The Division Leader's responsibility is to ensure that all activities performed by ERD at the Livermore Site and Site 300 are performed safely and comply with all pertinent regulations and procedures, and provide the necessary equipment and resources to accomplish the tasks described in this procedure.

5.2 Field Personnel

The field personnel are responsible for the safe completion of evacuating and containing purge water from monitoring wells as well as properly collecting samples according to guidelines set forth by all applicable SOPs. The wells to be sampled on a regular basis are declared in the quarterly Routine Sampling Schedule provided by the sampling coordinator (SC).

5.3 Field Support Personnel

The field support personnel are responsible for providing necessary equipment, collection devices and general field support which enables personnel to perform field activities in a timely and efficient manner.

5.4 Sampling Coordinator (SC)

The SC's responsibility is to supply a quarterly Routine Ground Water Sampling Schedule (also referred to as a Sampling Plan). In addition to providing an overall sampling plan, the SC has the option to provide a specific sample plan for each day (Daily Operations Guide). The technical information required for purging wells is also provided by the SC in the Well Specification Table.

Procedure No. ERD SOP-2.6	Revision Number 2	Effective Date December 1, 1995	Page 3 of 7
------------------------------	----------------------	------------------------------------	-------------

6.0 PROCEDURE

The growing concern over the past several years over low levels of VOCs in water supplies has led to the development of highly sophisticated analytical methods that can provide detection limits at part-per-trillion levels. Because the laboratory methods are extremely sensitive, well controlled, and quality assured, they cannot compensate for a poorly collected sample. The collection of samples should be as sensitive, highly developed, and quality assured as the analytical procedures. The proper collection of a sample for dissolved VOCs requires minimal disturbance of the sample to limit volatilization and, therefore, a loss of constituents from the sample.

6.1 Office Preparation

- 6.1.1 Prior to commencement of field activities, personnel shall review the appropriate Site Safety Plan, Quality Assurance Project Plan, and all applicable SOPs and OSPs. Current copies of all applicable documents shall be retained in the sample vehicle at all times.
- 6.1.2 Review all pertinent sampling information, such as the quarterly Routine Sampling Schedule and Well Specification Table provided by the SC.

The Routine Sampling Schedule contains the following information:

- Well to be sampled.
- Requested analyses.
- Contract analytical laboratory to which samples are to be sent to for analyses.
- Estimated amount of purge water to be collected, and where and how it will be treated.

Well Specification Table contains the following information:

- Type and size of pump.
- Casing depth and diameter.
- Screened interval.
- Discharge rate.

- 6.1.3 Obtain appropriate data collection forms, i.e., Chain-of-Custody (CoC) forms, Ground Water Sampling Logs (SOP 2.1, "Presample Purging of Wells," Attachment A), assigned field logbook, and any necessary shipping forms. Instructions for completing the log book entries and field forms are provided in SOP 4.2, "Sampling Control and Documentation."
- 6.1.4 The number and appropriate sample containers necessary for sampling should be obtained from the SC's supply. For VOC samples, EPA Level 1 40-mL VOA vials with certification and Teflon-lined septa are required (SOP 4.3, "Sample Containers and Preservation"). The SC replenishes sampling supplies from either the CAL or LLNL stores.
- 6.1.5 Field personnel should check sampling supplies (i.e., bottles, gloves, etc.) and inform the SC when the supply is low. Field personnel may reorder from the contract analytical laboratory (CAL) or LLNL stores.

Procedure No. ERD SOP-2.6	Revision Number 2	Effective Date December 1, 1995	Page 4 of 7
------------------------------	----------------------	------------------------------------	-------------

- 6.1.6 Field personnel should notify the SC when collecting interlaboratory collocated samples, so that arrangements can be made with the CAL courier for sample pickup.
- 6.1.7 Field personnel should notify the SC when collecting samples on a rush turn-around time (i.e., 24 to 48 hours). When samples are collected, the SC should inform the CAL ahead of time to allow for preparation.
- 6.1.8 The Administrative Escort Services must be given a 24-hour notice before work is scheduled in restricted areas. If appropriate, arrange access to sampling areas through Building Supervisors or the Control Point Operator per SOP 4.1, "General Instructions for Field Personnel."
- 6.1.9 Purge Water Collection:

- A. Site 300

The SC and field support personnel must ensure that wells have sufficient collection drums available at the well head for purge water containment (SOP 4.7B, "Site 300 Treatment and Disposal of Well Development and Well Purge Fluids"). The quantity of purge water to be collected for each well is listed in the Routine Sampling Schedule.

- B. Livermore Site

The SC will provide a specific order of wells to be sampled, in order to efficiently coordinate placement of presample purge water collection tankers. Tankers and drums containing purge water may not be left at the well location and will be logged and disposed of according to SOP 4.7A, "Treatment and Disposal of Well Development and Well Purge Fluids."

6.2 Field Preparation

- 6.2.1 Ensure that all sampling equipment is decontaminated according to SOP 4.5, "General Equipment Decontamination".
- 6.2.2 Compile all necessary equipment and instrumentation for sampling according to Attachment A, Equipment Checklist in SOP 2.1. When sampling for VOCs ensure that a sufficient number of 40-mL VOA vials with Teflon-lined septa are available to complete a sampling event.
- 6.2.3 Fill out initial information on the Ground Water Sampling Log and Water Sampling Logbook per instructions in SOP 4.2.
- 6.2.4 Organize sampling route:
 - A. Site 300
 1. Complete an entire Study Area (SA) before starting the next.
 2. Sample all clean wells within an SA first.
 3. Proceed to sample wells working from the least contaminated to the most contaminated.
 - B. Livermore Site
 1. The SC will specify area and order of well sampling (if needed).

Procedure No. ERD SOP-2.6	Revision Number 2	Effective Date December 1, 1995	Page 5 of 7
------------------------------	----------------------	------------------------------------	-------------

6.3 Operation

- 6.3.1 Purge well prior to sampling as specified in SOP 2.1. Obtain water quality parameters in accordance with SOP 2.2, "Field Measurements on Surface and Ground Waters." Ensure that the well was not pumped dry (see SOP 2.3, regarding low-yielding aquifers) and that high flow rates were not employed to cause turbulence in the formation.
- 6.3.2 Sample retrieval systems suitable for the valid collection of volatile organic samples are positive displacement bladder pumps, gear-driven submersible pumps, and bailers (Nielsen and Yeates, 1985; Barcelona et al., 1984). Field conditions and other constraints will limit the choice of appropriate systems. The focus of concern must remain the collection of a valid sample for analysis, which is a sample that has been subjected to the least amount of turbulence possible.

A. Sample Retrieval-Bladder Pump

These pumps are ideal for wells producing a sustainable yield of <1.0 gallons per minute (gpm), where the casing depth does not exceed 150 ft, and where there is not a significant quantity of water to remove (>100 gal). These pumps require a power supply and a compressed gas supply or compressor. They may be operated at variable flow (under 0.5 gpm) and pressure rates, making them acceptable for purging and sampling wells in low-yielding aquifers.

1. Label vials with appropriate sample information. Open vials and set caps in an upright position in a clean place. Collect the sample during the middle of the cycle. Collect one VOA vial at a time to avoid spillage and possible breakage. Sample should be collected over a collection vessel such as a tray, bucket or collection drum to avoid spillage to ground.
2. Hold the edge of the sample line at the top edge of the sample vial and allow the water to run down the inside into the vial. Do not allow the sample line to touch the sample vial or the water to drop or fall into the vial; avoid splashing. The proper collection of a sample for dissolved VOCs requires minimal disturbance of the sample to limit volatilization and, therefore, a loss of VOCs from the sample.
3. Fill the vials to just overflowing. Do not rinse the vials or excessively overflow them. There should be a convex meniscus on the top of the vials.
4. Check that the caps have not been contaminated (splashed) and carefully cap the vials. Place the caps directly over the top and screw down firmly. Do not over-tighten and break the cap.
5. Invert the vials and tap gently. If an air bubble appears, discard the vial and begin again. No entrapped air should be left in the sample vial. In some instances, a well can have natural off-gassing which can produce air bubbles in the sample. In these cases of natural off-gassing, the sample needs to sit open for approximately one minute to allow the sample to coalesce, and then top off the sample again to produce a sample without air bubbles.
6. Place the samples in airtight plastic bags on their sides (not straight up) in a cooler containing double-bagged ice, loose cubes, or bagged Blue ice. Loose ice should be replaced with double-bagged ice or bagged blue ice

Procedure No. ERD SOP-2.6	Revision Number 2	Effective Date December 1, 1995	Page 6 of 7
------------------------------	----------------------	------------------------------------	-------------

before shipping. Samples should be maintained at $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$. Include a temperature blank for the analytical laboratory.

B. Sample Retrieval—Submersible Pump

Electric submersible pumps are used to quickly and efficiently purge large quantities of water. The flow rate is controlled at the surface by an in-line ball valve attached to a sample tee. Samples are collected from a small diameter Teflon tube on the opposite side of the sample tee. The sampling flow rate is controlled by a needle valve. Although the needle valve provides good control of discharge rate, care must be exercised when sampling for VOCs to avoid possible splashing and aeration. Some electric submersible pumps are controlled by a rheostat mechanism to allow for better control and much lower discharge rates.

1. Place the generator downwind from the well. If the well is expected to dry out, a pump protector, such as a Coyote, can be used. This will automatically shut down the pump should the well be in danger of drying out. If a pump protector is not used, water levels should be monitored frequently to ensure the water level does not drop below the pump intake or screened interval.
2. Attach the dedicated sample tee (found inside the protective steel casing) to the discharge pipe. Plug the control box into the generator and start the generator. Adjust the discharge rate by partially closing the ball valve on the sample tee so that the well will yield water without exposing the screen. If using a rheostat equipped pump, the discharge rate is controlled by the pump speed control knob on the controller unit.
3. Follow steps 6.3.2A 1 through 6.

C. Sample Retrieval—Bailers

It is preferable to use a bailer constructed of Teflon or stainless steel. However, polyvinyl chloride (PVC) bailers are acceptable for well purging, although they should not be used to sample wells. An equipment blank sample should always be collected when using a portable purging device. The sample should be collected for VOCs after decontamination is completed and prior to placing the equipment downhole according to SOP 4.9, "Collection of QC Samples."

1. The retrieval line should be securely attached to the bailer. If nylon or cotton rope is used, tie a bowline knot.
2. Gently lower the bailer into the well and begin water removal. Avoid unnecessary agitation of the water.
3. A water level indicator or tape measure should be lowered by the bailer into the well to ensure that samples are retrieved from the middle of the screened section of a well.
4. To collect a sample from the bailer, a bottom emptying device is inserted into the bottom of the bailer which expels the water. Again, use caution when filling sample VOA vial (SOP 2.4, "Sampling Monitoring Wells with a Bailer").
5. Follow steps 6.3.2A 1 through 6.

Procedure No. ERD SOP-2.6	Revision Number 2	Effective Date December 1, 1995	Page 7 of 7
------------------------------	----------------------	------------------------------------	-------------

6.4 Post Field Operation

- 6.4.1 Prior to leaving the sampling location, cross check the samples with those requested by the SC and note any discrepancies.
- 6.4.2 Prior to sampling another site, thoroughly decontaminate all nondedicated equipment to prevent cross contamination by equipment (refer to SOP 4.5).
- 6.4.3 Complete the appropriate Ground Water Sampling Log and record sampling information into the designated Water Sampling Logbook per SOP 2.1 and SOP 4.2.
- 6.4.4 Ensure that the appropriate data are entered in the well log, and the well discharge line, sounding ports, sample tee, and well logbook are stored in their proper locations. Replace the lid and lock casing.
- 6.4.5 Verify that the CoC is appropriately completed per SOP 4.2. Indicate any special instructions in the Remarks Section of the CoC. Such instruction may include filtering and preserving the sample upon receipt. Also, for wells that are listed on the sampling plan as Clean Wells or for any well that is expected to be free of contamination write, "Verify any positive detections and call _____." The blank should be filled in with the appropriate QC Chemists name and phone number.
- 6.4.6 Deliver all samples daily to the appropriate lock box or SC for transport to the analytical laboratory.

6.5 Office Post Operation

- 6.5.1 Deliver all field logbook notes, ground water sampling logs, and CoC forms weekly to the SC. Deliver or fax copies of completed CoCs daily to the SC.
- 6.5.2 The SC will retain a copy of the original forms (CoC, ground water sampling log), and provide the originals to the Data Management Group (DMG) for final archive. The DMG will provide copies of the forms to the appropriate Operations and Regulatory Affairs Division Analyst, as necessary.

7.0 QA RECORDS

- 7.1 Ground Water Sampling Log
- 7.2 Logbooks
- 7.3 Chain-of-Custody Form

8.0 ATTACHMENTS

Not applicable.